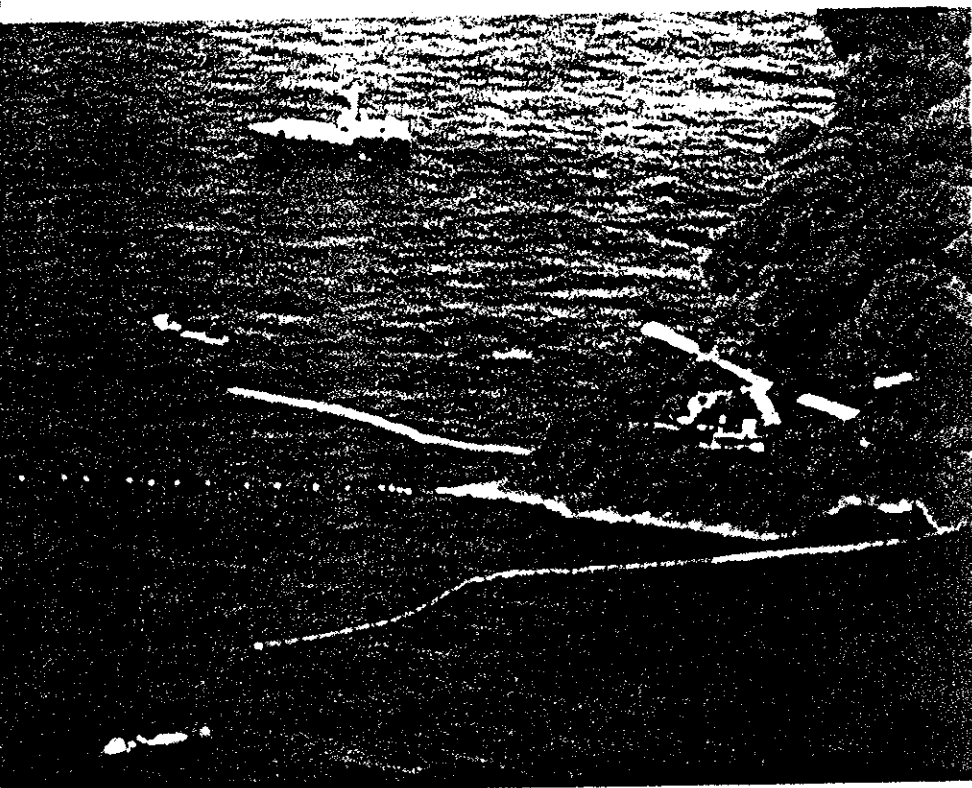


VOLUME 1

PROCEEDINGS OF THE
SEVENTEENTH ARCTIC AND
MARINE OIL SPILL PROGRAM
(AMOP) TECHNICAL SEMINAR

COMPTE RENDU: 17^e COLLOQUE
TECHNIQUE DU PROGRAMME DE LI
CONTRE LES DÉVERSEMENTS
D'HYDROCARBURES EN MER ET DA
L'ARCTIQUE (AMOP)



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(at the same temperature). This will be true of all fresh crude oils, and most fuel oils, for both salt and fresh water. Bitumens and certain residual fuel oils may have densities greater than 1.0 g/mL and their buoyancy behaviour will vary depending on the salinity and temperature of the water. The density of spilled oil will also increase with time, as the more volatile (and less dense) components are lost. After considerable evaporation the density of some crude oils may increase enough to cause the oils to sink below the water surface.

Two density-related properties of oils are often quoted: specific gravity and American Petroleum Institute (API) gravity. Specific gravity (or relative density) is the ratio, at a specified temperature, of the oil density to the density of pure water. A specific gravity less than 1.0 indicates that the oil will float. The API gravity scale arbitrarily assigns an API gravity of 10° to pure water. API gravity is calculated as:

$$\text{API Gravity (}^\circ\text{)} = \frac{141.5}{\text{Specific Gravity (60/60 }^\circ\text{F)}} - 131.5$$

Oils with low densities, and hence low specific gravities, have high API gravities. The price of a crude oil is usually based on its API gravity, with high gravity oils commanding higher prices. API gravity and density or specific gravity at 15 °C can be interconverted using Petroleum Measurement Table 3 (American Petroleum Institute 1982).

At ESD, density is ordinarily measured using an Anton Parr DMA 48 digital density meter, and following ASTM method D 5002 - *Density and Relative Density of Crude Oils by Digital Density Analyzer* (ASTM 1993). A constant temperature is maintained by a HAAKE controlled temperature circulator. Using the DMA 48, densities can be measured to 0.0001 g/mL with a repeatability of ± 0.001 g/mL. Occasionally, for very heavy oils or bitumens, a Gay-Lussac density bottle is used, at elevated temperatures if necessary. Under these conditions the density is reported to 0.001 g/mL with a repeatability of ± 0.01 g/mL.

Viscosity

Viscosity is a measure of a fluid's resistance to flow; the lower the viscosity of a fluid, the more easily it flows. Like density, viscosity is affected by temperature. As temperature decreases, viscosity increases. Viscosity is a very important property of oils because it affects the rate at which spilled oil will spread, the degree to which it will penetrate shoreline substrates, and the selection of mechanical spill countermeasures equipment.

Viscosity measurements may be absolute or relative (sometimes called 'apparent'). Absolute viscosities are those measured by a standard method, with the results traceable to fundamental units. "Absolute viscosities are distinguished from relative measurements made with instruments that measure viscous drag in a fluid, without known and/or uniform applied shear rates." (Schramm, 1992). An important benefit of absolute viscometry is that the test results are independent of the particular type or make of viscometer used. Absolute viscosity data can be compared easily between laboratories worldwide.

There are several ASTM Standard Methods for measuring the viscosity of oils. These include D 445, D 2983, D 4741, D 4486, and D 5133 (ASTM 1993). Of these,

only methods D 445 and D 4486 will yield absolute viscosity measurements. Both of these methods make use of glass capillary kinematic viscometers and will produce absolute measurements in units of centistokes (cSt) only for oils which exhibit Newtonian flow behaviour (viscosity independent of the rate of shear). Unfortunately, no ASTM standard method exists which makes use of modern rotational viscometers capable of making absolute viscosity measurements for both Newtonian and non-Newtonian fluids at a variety of well-controlled, known and/or uniform shear rates.

The system used by ESD for the routine measurement of dynamic viscosity is comprised of the HAAKE RV20 Rotovisco with the M5 measuring system, SV1 and NV sensors, and HAAKE RC20 Rheocontroller. The Rheocontroller, which is connected to a personal computer, allows the shear rates to be controlled with great accuracy and precision. A dedicated software package performs automatic dynamic viscosity measurements and outputs the stored data in table and graphical formats. The SI unit of dynamic viscosity is the millipascal-second (mPa·s). This is equivalent to the former unit of centipoise (cP). In general, the viscosity values obtained using this system will be repeatable to $\pm 5\%$ of the mean.

The detailed procedures used for viscosity measurements on oils and emulsions are as follows:

1.0 Procedure for oils

- 1.1 The sample is removed from cold storage and shaken for 15 minutes.
- 1.2 A rotor and cup are chosen based on visual observation of the oil sample after shaking: See Table 1.

Table 1 HAAKE Rotovisco Cup and Rotor Characteristics

Sensor (rotor)	NV	SV1
Cup	NV	SV
Application	Low viscosity	High viscosity
Viscosity range (cP)	1 - 10 ⁴	50 - 10 ⁶
Volume (mL)	9	9

- 1.3 Using a syringe, an aliquot of oil of appropriate volume (see Table 1) for the chosen cup and rotor is obtained. If the oil is too viscous to be pulled into the syringe, it may be sampled by removing the plunger, cutting off the end of the syringe, and plunging the syringe into the oil. The excess oil is wiped off from the outside of the syringe and the sample cup is carefully filled.
- 1.4 The sample cup is placed into the holding container. A visual check is made to determine if there is sufficient sample (up to the top of the rotor) or excess sample (over the top of the rotor). The amount of sample is adjusted as necessary.
- 1.5 The sample is allowed to equilibrate at the chosen temperature; 30 minutes at 15 °C or 45 minutes at 0 °C.

1.6 The measurement parameters are set:

Shear rate: for Newtonian oils, 200/s for the SV1 rotor and 400/s for the NV rotor. Non-Newtonian oils are run at 1/s and 10/s. In special cases (e.g. intercalibration tests), the shear rate is set as specified in the test protocol.

Ramp program: Ramp up, 5 minutes. Hold 5 minutes. Ramp down, 5 minutes.

When the run is complete, the data are printed out along with a plot of viscosity versus shear rate.

1.7 The rotor and cup are removed and cleaned using sorbents and dichloromethane.

2.0 Procedure for Water-in-Oil Emulsions

Water-in-oil emulsions are non-Newtonian fluids. As such, viscosity measurements on emulsions are performed in the same manner as those on non-Newtonian oils, with the following differences:

2.1 The prepared emulsion is not shaken prior to measurement of viscosity.

2.2 If the emulsion has been prepared and/or stored at the measurement temperature, the equilibration times may be shortened to ten minutes.

Pour Point

The pour point of an oil is the lowest temperature at which the oil will just flow, under standard test conditions. The failure to flow at the pour point is usually attributed to the separation of waxes from the oil, but can also be due to the effect of viscosity in the case of very viscous oils. Also, particularly in the case of residual fuel oils, pour points may be influenced by the thermal history of the sample, i.e. the degree and duration of heating and cooling which the sample has been exposed to. From a spill response point of view, it must be emphasized that the tendency of the oil to flow will be influenced by the size and shape of the containers, the head of the oil, and the physical structure of the solidified oil. Hence the pour point of the oils is an indication, and not an exact measure, of the temperature at which flow ceases (Dyroff 1989).

A modified version of ASTM method D 97 - *Standard Test Method for Pour Point of Petroleum Oils* (ASTM 1993) is used for pour point determinations at ESD. The oil is removed from cold storage and shaken for 15 minutes. If the oil is not fluid at the storage temperature it is warmed until fluid and then shaken briefly by hand. The oil is then poured into test jars meeting the specifications of ASTM method D97. Duplicate samples of each oil are tested. The test jars are fitted with stoppers and thermometers and warmed in a water bath to 45-50 °C. The samples are then removed from the bath and cooling takes place in the following manner. First, the samples are allowed to cool to room temperature. If additional cooling is required, the samples are moved sequentially to a cold room maintained at 10 °C, a refrigerator at 0 °C, a freezer at -30 °C, and finally to an acetone/dry ice bath at approximately -65 °C. As the sample is cooling, it is checked periodically to see if the pour point has been reached. These checks are made as per ASTM method D97, but not necessarily at intervals which are multiples of 3 °C. When the pour point has been reached, 3 °C is added to the temperature recorded from the thermometer, as specified in the ASTM method. This value is reported as the pour point.

Flash Point

The flash point of a fuel is the temperature to which the fuel must be heated to produce a vapour/air mixture above the liquid fuel which is ignitable when exposed to an open flame under specified test conditions. In North America flash point is used as an index of fire hazards. As such, shipping regulations use flash point as a criterion to establish labelling requirements. Likewise, flash point is an extremely important factor in relation to the safety of spill cleanup operations. Gasolines and other light fuels can be ignited under most ambient conditions and therefore pose a serious hazard when spilled. Many freshly spilled crude oils also have low flash points until the lighter components have evaporated or dispersed.

There are several ASTM methods for measuring flash points. Methods D 93/IP 34 - *Standard Test Methods for Flash Point by Pensky-Martens Closed Tester* and D 56 - *Standard Test Method for Flash Point by Tag Closed Tester* are the most commonly used (ASTM 1993). The Pensky-Martens tester has an integral stirrer, but no cooling bath. The minimum flash point which can be determined by method D93/IP34 is 10 °C. The Tag closed tester has an integral cooling bath, but no stirring mechanism. Method D 56 is intended for liquids with a viscosity less than 9.5 cSt at 25 °C and a maximum flash point below 93 °C. Many fresh crude oils have flash points below 10 °C, but viscosities above 9.5 cSt at 25 °C. For this reason, ESD has chosen to use a SUR Berlin TAG 2 automatic flash point tester which has been modified by adding a stirring mechanism. The mechanism operates in a similar fashion to that found on a Pensky-Martens tester, but is of a more efficient design, using a propeller rather than a paddle. The stirrer aids in producing more uniform heat transfer to oils which exceed the design viscosity, and in no way interferes with the test mechanism. Flash points measured by this instrument are generally repeatable to ± 4 °C.

Interfacial Tension

Interfacial tension is the force of attraction between the molecules at the interface of two fluids. At the air/liquid interface this force is often referred to as surface tension. The SI units for interfacial tension are milliNewtons per metre (mN/m). These are equivalent to the former units of dynes per centimetre (dyne/cm).

The surface tension of an oil, together with its viscosity, affects the rate at which an oil spill spreads. Air/oil and oil/water interfacial tensions can be used to calculate a spreading coefficient which gives an indication of the tendency for the oil to spread. It is defined as:

$$\text{Spreading Coefficient} = S_{WA} - S_{OA} - S_{WO}$$

where: S_{WA} is water/air interfacial tension
 S_{OA} is oil/air interfacial tension
 S_{WO} is water/oil interfacial tension

Spreading to a thin slick is likely if the spreading coefficient of an oil is greater than zero, and the higher the spreading coefficient the faster the spreading will occur (Twardus 1980).

Unlike density and viscosity, which show systematic variations with temperature and degree of evaporation, interfacial tensions of crude oils and oil products show no such correlations. Neither does interfacial tension of these substances show any correlation to viscosity (Jokuty et al. 1994).

A single ASTM method, D 971 - *Standard Test Method for Interfacial Tension of Oil Against Water by the Ring Method* (ASTM 1993), is applicable to the measurement of oil/water interfacial tensions. At ESD, interfacial tension measurements are now made using a Kruss Digital Tensiometer K10ST. This instrument uses the Du Nouy principle for measuring interfacial tension, as recommended in the ASTM method. It is operated in accordance with the manufacturer's directions. Unlike manually operated ring tensiometers, the maximum deformation of the lamella is detected electronically, and occurs before the ring pulls completely through the interface. This results in interfacial tensions which are slightly lower than those measured manually. Samples are run in duplicate. Repeatability is $\pm 2\%$ of the mean.

Evaporation

Evaporation is a major process which contributes to the weathering of spilled oil. While pure compounds evaporate at constant rates, oils, which are composed of thousands of compounds, do not. Rapid initial loss of the more volatile fractions is followed by progressively slower loss of less volatile components. Evaporation of 25% of the total volume of a spilled crude within one day of the spill is not uncommon (Fingas, Duval and Stevenson 1979).

Evaporative loss results in significant changes in the physical properties and chemical composition of spilled oils. These changes in turn influence choices which must be made relating to oil spill countermeasures. For this reason, it is desirable to produce evaporated oils and to determine their physical properties. A protocol has been developed for the production of such samples using rotary evaporation at ambient pressure. An oil is first evaporated at 80 °C for 48 hours. At this point the rate of evaporation will have decreased to less than one percent (mass) per day. The sample is weighed periodically throughout the 48 hours and again at the end. The total mass percent lost is determined and then the process is repeated at a minimum of two intermediate evaporative loss values. The detailed procedure is as follows:

3.0 Rotary Evaporation of Oils

The apparatus used is a Wheaton N10 rotary evaporator with a 10 L flask and an integral water bath (capacity 14 L). The bath temperature can be controlled to ± 0.5 °C. The thermo control range is 1 °C to 120 °C. The rotation speed can be continuously varied from 10 to 135 rpm.

- 3.1 The water bath is filled with distilled water and brought to 80 °C. Higher temperatures are avoided to ensure that cracking of oil components does not take place. The temperature should remain constant throughout the evaporation process.
- 3.2 The oil is removed from storage and shaken for 15 minutes. Two litres of oil is placed into the tared 10 L flask.

- 3.3 The flask is placed on the evaporator and run at full speed (135 rpm). An air flow of approximately 13 L/min through the flask is maintained by leaving the vacuum release stopcock open to atmospheric pressure.
- 3.4 The flask is reweighed every half hour for the first hour, every hour up to eight hours, every two hours up to 16 hours, every four hours up to 32 hours, and every eight hours up to 48 hours. Small samples (≤ 1 mL), totalling less than 10 mL, may be removed at any time without recalculating the weight percent lost, as they will not significantly affect the results.
- 3.5 If evaporation must be stopped (e.g. scheduled power or water outage, overnight, weekends), the flask must be sealed tightly and refrigerated. When the run is restarted, the flask should be removed from the cold and allowed to sit at room temperature while the water bath is returned to operating temperature.

Dispersibility

The Swirling Flask Test, used for determining the chemical dispersibility of oils, was developed at ESD. Details of the apparatus and procedures are given in the literature (Fingas et al. 1989a). Studies have also been done to determine the effects of oil-to-water ratios and settling times (Fingas et al. 1989b) and energy (Fingas et al. 1991; Fingas, Kyle, and Tennyson 1992; Fingas, Kyle, and Tennyson 1993).

Hydrocarbon Groups

The behaviour of crude oils at sea is dominated by their chemistry. The main constituents of crude oils can be grouped into several broad classes of compounds: saturates, aromatics, resins and asphaltenes.

Saturates are alkanes with structures of C_nH_{2n+2} (aliphatics) or C_nH_{2n} in the case of cyclic saturates (alicyclics). Small saturates ($< C_{18}$) are the most dispersible components of oils. Large saturates (waxes) can produce anomalous evaporation, dispersion, emulsification and flow behaviours.

Aromatics are compounds that have at least one benzene ring as part of their chemical structure. The small aromatics (one and two rings) are fairly soluble in water, but also evaporate from spilled crude rapidly. Larger aromatics show neither of these behaviours to any extent.

Resins and asphaltenes are similar in many ways. Asphaltenes can be thought of as large resins. Both groups are thought to be composed of condensed aromatic nuclei which may carry alkyl and alicyclic systems containing heteroatoms such as nitrogen, sulphur, and oxygen. Metals such as nickel, vanadium and iron are also associated with asphaltenes. Both groups do not appreciably evaporate, disperse or degrade, and both groups stabilize water-in-oil emulsions when they are present in quantities greater than 3% (Fingas 1993).

Asphaltenes and waxes are the only hydrocarbon groups routinely determined at ESD. Methods are under development which will allow the determination of saturates, aromatics, and resins as well (see below: Methods Under Development - Hydrocarbon Groups). These new methods may also replace the old precipitation methods currently used to separate asphaltenes and waxes from the oil. The detailed procedures used for these separations follow. In these procedures the term 'maltenes' refers to the deasphalted oil.

4.0 Determination of Asphaltenes

- 4.1 The oil is shaken for ½ hour prior to sampling.
- 4.2 Using a syringe, 5 mL of oil is weighed by difference. The oil is placed in a 500 mL Erlenmeyer flask with a glass stopper.
- 4.3 15 mL of toluene is added to the flask which is then stoppered and swirled gently for ½ hour on a shaker.
- 4.4 200 mL of pentane is added. The flask is again stoppered, swirled for ½ hour, and then allowed to stand overnight at room temperature.
- 4.5 A 0.45 µm organic solvent resistant filter membrane and weighing boat are weighed to 0.0001 g.
- 4.6 The asphaltenes are filtered from the toluene/pentane mixture using a glass filtration unit and the previously weighed filter membrane. A vacuum is applied, not exceeding 380 mm Hg to avoid the loss of pentane through the pump. The flask is rinsed repeatedly with pentane and any asphaltenes adhering to the glass are scraped into the filtering apparatus with a rubber policeman.
- 4.7 Air is aspirated through the sample for approximately one minute until the sample has a cracked, dry appearance.
- 4.8 The filter membrane is removed from the apparatus and placed in the previously weighed boat. Care must be taken as in some cases a static charge may develop which can result in loss of sample. The boat and membrane are placed in a vacuum desiccator overnight. Care must be taken both when evacuating and releasing the vacuum so as not to disturb the samples.
- 4.9 The recovered filtrate is transferred to a round-bottom flask. The solvents will be removed and the waxes will be precipitated from the recovered maltenes.
- 4.10 The boat and membrane are weighed to 0.0001 g and the amount of asphaltenes recovered is determined as a weight percent of the oil used.

5.0 Determination of Waxes

- 5.1 Using the filtrate recovered during the determination of asphaltenes, the solvents are removed by rotary evaporation at 30 °C (to remove pentane) and 80 °C to remove toluene.
- 5.2 The maltenes are transferred into a 250 mL Teflon Erlenmeyer flask using 50 mL of a 1:1 volume mixture of dichloromethane (DCM) and methyl ethyl ketone (MEK). The flask is stoppered and swirled for ½ hour.
- 5.3 A Buchner funnel is weighed to 0.0001 g. Then the funnel, the Teflon flask, the filtering flask, and a squeeze bottle of DCM/MEK are chilled overnight at -30 °C.
- 5.4 Before filtering, a Whatman GF/C 5.5 cm glass microfibre filter is weighed to 0.0001g.
- 5.5 Working as quickly as possible, the chilled filtering apparatus is set up. The filter is wetted with the chilled DCM/MEK solution and the vacuum pump is turned on at maximum. The oil solution is filtered quickly to avoid warming and possible dissolution of the precipitated waxes. Extra care is taken to pour the solution into the centre of the filter. The Teflon flask is rinsed with chilled DCM/MEK which is then poured onto the filter.
- 5.6 Aspiration is continued for five minutes.

- 5.7 The funnel and filter are allowed to dry under a fume vent and then placed in a vacuum desiccator overnight.
- 5.8 The funnel, filter and waxes are weighed and the amount of waxes recovered is determined as a weight percent of the oil used.

Methods Under Development

Aqueous Solubility

Some components of oils spilled on water can enter the environment via the process of dissolution. In general, the amount of soluble compounds is small, less than 50 mg/L (Bobra 1992), but under certain conditions this small amount can have a significant effect on organisms which live or reproduce in the affected waters.

Based on the work of Bobra (1992), a method is under development which uses a headspace analyzer coupled to a gas chromatograph (GC) with mass selective detection (MSD). The exact method to be used to prepare the water-soluble fractions (WSF) is still under development. It is anticipated that the final protocol will make use of 40 mL amber Pierce vials. These will be completely filled with water (fresh or salt) and sealed with teflon-lined septa and screw caps. A volume of oil will be injected by syringe into the inverted vial while allowing water to be displaced through a second syringe needle inserted through the septum.

The effects of oil-to-water ratio, agitation, dissolution time, and temperature are under investigation. Of these parameters it is felt that oil-to-water ratio is the most important. From the results of Bobra (1992) it seems that oil-to-water ratios greater than 1:100 will result in dissolved organics values which are too high as a result of the phenomenon of co-solubility. That is, at high oil loadings the concentrations of some organic compounds are sufficiently high that they may dissolve in each other, as well as in the water. On the other hand, if the oil-to-water ratio is less than 1:1000, the resulting dissolved organics values will be too low and will again not reflect the true aqueous solubility.

At the end of the dissolution time a 10 mL water sample is obtained by syringe and transferred to a 20 mL headspace vial. The sample is analyzed using static headspace sampling and GC/MSD. Details of the analysis are given in Li et al. (1994). Using this technique it is possible to determine not only benzene, toluene, ethylbenzene, and xylenes (BTEX) but also C₅- and C₆-substituted benzenes, naphthalene, and C₅- to C₁₅-alkanes.

Boiling Range Distribution

In the oil refining industry boiling range distribution data are used to evaluate new crudes, to confirm crude quality before purchase, to monitor crude quality during transportation, and to provide information for the optimization of refinery processes. From the point of view of oil analysis for environmental purposes, boiling range distributions provide an indication of volatility and component distribution. In addition this data can be used as input to some oil spill modelling programs. Boiling range distribution data may also prove to be useful in the development of equations for predicting evaporative loss.

Traditionally, boiling range distributions have been determined by distillation. Atmospheric and vacuum distillation techniques have largely been replaced by 'simulated' distillation methods. These methods use low resolution gas chromatography and correlate retention times to hydrocarbon boiling points. ASTM methods D 2887 - *Standard Test Method for Boiling Range Distribution of Petroleum Fractions by Gas Chromatography* and D 3710 - *Standard Test Method for Boiling Range Distribution of Gasoline and Gasoline Fractions by Gas Chromatography* use external standards composed of n-alkanes (ASTM 1993). ASTM method D 5307 - *Standard Test Method for Determination of Boiling Range Distribution of Crude Petroleum by Gas Chromatography* is very similar to D 2887 but requires two runs to be made with each sample, one of which uses an internal standard (ASTM 1993). The amount of material boiling above 538 °C (reported as residue) is calculated from the differences between the two runs.

While these ASTM methods do not preclude the use of capillary columns, they have generally made use of packed columns. The use of capillary columns has many advantages over packed columns: (a) more stable baselines; therefore fewer blank, calibration and quality control runs are required, (b) instruments require less maintenance, (c) better column to column consistency, (d) calibration beyond 615 °C, (e) longer column life, (f) column quickly changed and conditioned. An alternative method for the simulated distillation of whole crudes by capillary gas chromatography has been developed by researchers at Imperial Oil (Workman et al. 1994). The method requires high temperature capillary GC instrumentation and a special aluminum clad column which has a very thin film of stationary phase (0.1 µm).

ESD is in the process of acquiring an AC Analytical Controls SIMDIS ChemStation® Analyzer which will allow the implementation of the method developed by Workman et al (1994). This system will be provided with dedicated simulated distillation software that will control all events within the analytical system and perform all data calculations and reporting. The AC SIMDIS software will cover ASTM methods D 2887 and D 3710. In addition a method designated AC SIMDIS 750, which has been proposed as an ASTM standard method, will be used for residuals, non-residuals and crudes with a final boiling point up to 750 °C.

Evaporation Rate

While a protocol (described above) has been developed to produce quantities of evaporated oils for physical and chemical analyses, another protocol is being developed dedicated to the determination of evaporation equations for individual oils. The apparatus is simple and consists of a shallow pan set on top of a top-loading balance which has an RS-232 connection to a computer. Data acquisition software allows the weight to be determined at pre-programmed time intervals for as long as desired. Factors such as temperature, air speed and oil thickness are being studied. In general, a 'reasonably- steady-state' is reached in one day.

Emulsion Formation, Stability and Characterization

The formation of water-in-oil emulsions from crude oils spilled at sea has important implications for the fate and behaviour of the oil and its subsequent cleanup. It is desirable, therefore, to determine if an oil is likely to form an emulsion, and if so, whether that emulsion is stable, and what its physical characteristics are.

A method has been developed for the formation of water-in-oil emulsions. Unlike previous methods, such as that used by Mackay and Zagorski (1982), this method makes use of commercially available equipment. The advantage of this is that reproducibility is considerably improved. The apparatus used is the 8-place Rotary Agitator with variable speed motor (1.5-56 rpm) from Associated Design. This apparatus uses the same end-over-end type of rotation as used by Mackay and Zagorski (1982). The mixing vessels are Wheaton 2.2 litre wide mouth glass bottles. The water-to-oil ratio, the fill volume, and the orientation of the vessels were found to be important parameters affecting emulsion formation. The emulsion formation method, with these parameters optimized, is as follows:

6.0 Emulsion Formation Method

- 6.1 500 mL of salt water (3.3% w/v NaCl) is placed in each mixing vessel
- 6.2 20 mL of oil is added to each mixing vessel
- 6.3 The vessels are sealed and placed in the rotary agitator such that the cap of each mixing vessel will lead into the direction of rotation.
- 6.4 The vessels are rotated at 50 rpm for 3 hours.

Before a method is developed for determining the stability of water-in-oil emulsions, a specific criterion of stability is required. The term 'stability' implies a significant persistence of structure over time. To determine what physical property or properties might be used as such a criterion, emulsions of several different oils were formed as described above. These were stored for 14 days at 10 °C, with measurements made periodically of water content (weight percent) and viscosity. It was found that emulsions which had decreases of less than 5% in water content concurrent with viscosity increases to values greater than 100,000 cP were stable. Emulsions prepared from the same oils using a lower energy formation method were not stable. The low energy preparation method resulted in emulsions which lost greater amounts of water and had viscosities which increased very slightly over the 14 day period but which remained well under 100,000 cP. This energy dependence of emulsion stability is discussed in detail elsewhere (Fingas, Fieldhouse and Mullin 1994). The exact protocol for determining emulsion stability is still under development, but will likely make use of water content and viscosity data obtained over some set time period.

The work on emulsion stability has necessitated the acquisition of special equipment and subsequent development of appropriate techniques for determining the physical properties of emulsions. As discussed above, water content and emulsion viscosity are the two properties of most interest.

Water contents of emulsions are determined by Karl Fischer titration using a Metrohm 701 KF Automatic Titrator. The emulsion is sampled by syringe, its mass being determined by difference weighing. The sample is dissolved in a pre-titrated 1:1:2 volume mixture of methanol/chloroform/toluene and then titrated with standard pyridine-free Karl Fischer reagent. The water content is determined on a mass basis. Sampling provides the largest source of error. While multiple water content determinations on a single emulsion will have a standard deviation of approximately 0.2 weight percent, results which differ by ±1 weight percent are not considered to be significantly different.

One method for measuring emulsion viscosities has been discussed above (Methods in Use - Viscosity). In addition, a HAAKE RS100 Controlled Stress Rheometer has recently been acquired. The RS100 can be used as a controlled stress instrument as well as a controlled rate instrument. It can be used to make measurements of many interesting rheological properties such as shear thinning, viscoelasticity, thixotropy, and yield stress, which may prove to be useful in the characterization of emulsions and for environmental purposes.

Hydrocarbon Groups

Saturate, aromatic and polar compounds (described previously) can be determined using various techniques such as open column chromatography (ASTM D 1319, D 2007, D 2549), or thin layer chromatography with flame ionization detection (TLC/FID) (Ackman et al. 1990; Pollard et al. 1992). None of these methods are suitable for use with whole, fresh crudes due to restrictions on the boiling range. A possible solution to this problem would be to combine the data produced by two (or more) methods. An open column technique used for separating saturate and aromatic fractions of oils for subsequent analysis by GC/MS and GC/FID (Wang, Fingas, and Li 1993), could be extended to recover a polar fraction as well. Volatile components (lost during separation) and those masked by the hexane solvent, could be determined from a separate headspace analysis of the whole, fresh crude. Together these analyses could produce both a detailed analysis of the chemical composition of the oil and a summation of that data into hydrocarbon groups.

Surface Adhesion/Surface Washing

In past studies which have been done relating to the penetration of oils and emulsions into shoreline sediments (Humphrey and Harper 1993; Owens and Taylor 1993), a property of oils referred to as 'stickiness' has been identified as being an important parameter. To aid in further studies relevant to shoreline oiling, test methods are under development for two different measures of stickiness. The first of these has been designated the surface adhesion test. This test will produce a quantitative measure of the amount of oil that will adhere to a standard test surface. As presently conceived, the standard surface will be that of a full-scale penetrometer cone. Both an aluminum cone and the standard brass cone are under consideration. In either case, the cone will provide a known surface area which has been calculated to be 54.65 cm². By dipping the cone into an oil of interest and then weighing it until the oil ceases to drip off, it will be possible to compare oils on the basis of both the rate at which the oil drips off (this will be related to the viscosity), and the amount of oil which remains on the standard surface (g/m²). In a preliminary test done with a flat piece of stainless steel (6.5 cm square, 0.1 cm thick) slightly more than 2 grams of Bunker C remained on the stainless steel, resulting in a surface adhesion of 237 g/m².

The second test relating to oil stickiness will measure the amount of oil remaining on a standard test surface after washing with water (fresh or salt). This test will make use of the existing protocol for testing surface-washing agents (Fingas et al. 1994). For the testing of surface-washing agents, the standard oil is Bunker C. The new test will follow the surface-washing agent test procedure for blank runs, using the oil of interest. The full test method is described below.

7.0 Surface-Washing Agent Test

The standard test surface consists of a trough made from a 30 cm length of 1/4 inch (1.9 cm) stainless steel angle stock (90°). A stand with clamps is set up such that the trough can be held at an angle of 30 degrees from the horizontal with the lower end of the trough just clearing the edge of a 250 mL waste beaker that is set up to catch the runoff. The stand also holds a 50 mL syringe with an 18 gauge needle in a vertical position 2.5 cm above the trough at a point 21.5 cm from the trough's lower end.

- 7.1 Weigh a clean, dry trough. The trough should be at room temperature before weighing.
- 7.2 Dispense 150 µL oil onto the trough. The slick is positioned along the fold of the trough commencing approximately 16 centimetres from the lower end and moving upward in an even flowing motion for about 4.5 to 5 centimetres. Any oil remaining on the tip of the pipette can be removed by wiping the tip on the trough at a point just below the beginning of the slick.
- 7.3 Place the oiled trough on the balance. While waiting for a steady reading, start the clock/stopwatch/timer. Record the weight of the oiled trough and stand vertically after weighing.
- 7.4 At t=10 minutes, place 30 µL of washing agent onto the slick. This is accomplished by depressing the plunger of the pipette until a drop protrudes about halfway out of the tip. This drop is then touched to the oil slick. Repeat this technique in order to get a thin and even coating over the slick. Record the weight and place the trough in a horizontal position for 10 minutes.
- 7.5 At t=19:45 minutes, set up the trough in the stand as described above.
- 7.6 At t=20 minutes place 5 mL of fresh or salt water in the rinse dispensing syringe body. The water should then drip out of the needle onto the trough thus rinsing away the oil/washing agent mixture.
- 7.7 At t=30 minutes, repeat the rinse procedure.
- 7.8 At t=40 minutes, visually examine the trough to determine how much water remains on or in the oil slick (the water is fairly obvious). Small pieces of dampened Kimwipe can be used to blot water droplets without removing oil. Once all the water has been removed, the trough can be reweighed.
- 7.9 Calculations:

$$\text{Oil deposited} = \text{trough weight (freshly oiled)} - \text{clean dry trough weight}$$

$$\text{Oil removed} = \text{trough weight (freshly oiled)} - \text{rinsed blotted trough weight}$$

$$\text{Percentage of oil removed} = \frac{\text{Oil removed}}{\text{Oil deposited}} \times 100$$

Elevated temperature rinsing runs can be carried out in the same way except that the rinse water is warmed to the desired temperature. In all cases, blanks should be run using the same procedure but omitting step 7.4. That is, the surface-washing agent would not be applied at t=10 minutes; however, rinsing would still be done at t=20 and t=30 minutes.

After the final weighing is completed, the trough is cleaned by first wiping off the oil with small pieces of polypropylene sorbent pad and then rinsing successively with methylene chloride and acetone. The trough is wiped dry then placed in a drying oven for two to three minutes to remove all traces of solvent.

Conclusion

A growing awareness of, and concern for, our environment are creating the desire for more specific knowledge of the properties and behaviour of oil as they may impact our environment. Our analytical capabilities continue to grow as new and better instruments are developed. As technology will no doubt continue to improve the tools available to us, we can but also strive to improve our abilities to use those analytical tools to the best advantage. In this sense, we are obliged to continue to develop new methods and to try to perfect old ones, not merely when it is convenient to do so, but whenever it is possible to do so.

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